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Selective Separation of Palladium from Organic Solutions Containing Nickel or Platinum Using Polythioamide as a Sorbent

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Abstract The feasibility of the selective recovery of Pd from organic liquid waste using polythioamide (PTA) as a sorbent has been investigated. PTA effectively sorbed Pd(II) in some organic solutions under not only acidic conditions but also basic conditions. PTA was also able to sorb Pd from organic solutions containing $PdCl_2(PhCN)_2$ and $Pd_2(dba)_3$. The results for the molecular structure of a model compound ($[Pd(C_{11}H_{15}NS)_4]Cl_2$) suggest that the presence of a S donor plays an important role in the sorption of Pd(II) by PTA. The sorbed Pd was quantitatively eluted using 1,3-bis(diphenylphosphino)propane in MeOH, and the recovered PTA can be reused at least five times. The selective separation of Pd(II) was achieved even from organic solutions containing a 100 times larger amount of Ni(II) or Pt(IV) under acidic conditions or basic conditions, respectively.

Keywords Palladium separation, Polythioamide, Sorption, Elution with phosphine compound

1 Introduction

The recovery of precious metals from aqueous and organic liquid waste arising from the chemical, electronics, and plating industries has gained in importance from the viewpoint of the effective utilization of resources. The group 10 metals (Ni, Pd, and Pt) are widely used in these industries because of their specific physical and chemical properties. The catalytic activity and nobility of these metals have resulted in a wide range of applications in many fields in various chemical processes. The Pd-catalyzed carbon-carbon bond-forming reactions such as the Mizoroki-Heck and Suzuki-Miyaura coupling reactions are used in the production of fine chemicals [1]. However, the homogeneous catalytic systems usually require tedious and expensive workups to obtain a pure fine chemical product; in other words, the recovery of the precious metal is troublesome and time-consuming. Recently, several Pd-immobilized heterogeneous catalyst systems have been investigated with the aim of recovering the precious metal catalysts [2]; however, the durability of the catalysts and the leaching of precious metals, which are due to the instability of the immobilized metal complexes, still remain issues. Therefore, simple and selective techniques for recovering the precious metals from aqueous and organic liquid waste are desired.

Sorption using polymer sorbents is one of the most practical techniques in the recovery of metals from a solution. Although various sorbents have been developed and are now commercially available as metal scavengers [3], highly selective and effective separation techniques for organic liquid waste had limited success because of the interference by coexisting organic and inorganic constituents. Ishihara *et al.* reported that polystyrene-bound trimercaptotriazine is effective for removing Pd(II) from a THF solution [4].

We previously prepared polythioamide (PTA) by the Willgerodt-Kindler reaction [5]. The coordination chemistry of a secondary thioamide is intriguing because the

secondary thioamide group is involved in equilibrium with its amino-thione and imino-thiol tautomers, which modulates the donor ability of the thioamide group via the N-to-S backbone [6]. This situation prompted us to utilize PTA as a sorbent for group 10 metals in aqueous as well as organic solutions, and we found that Pd(II) could be effectively separated. PTA was able to sorb Pd(II) and its complexes in various aqueous and organic solutions under not only acidic conditions but also basic conditions. We here report the feasibility of the selective recovery of Pd(II) from organic liquid waste using PTA. Some of the results were reported in a previous communication [7].

2 Experimental

2.1 Materials and General Procedures

All reagents were purchased from commercial suppliers and used without any further purification. For the investigation of metal sorption in an aqueous solution and MeOH solution, a standard solution of each metal (1000 mg L^{-1}) was purchased from Kanto Chemical. In the standard solution, each metal was dissolved with 1 mol L^{-1} HNO_3 for Pd(II), 1 mol L^{-1} HCl and trace amount of HNO_3 for Pt(IV) and Au(III), or 0.1 mol L^{-1} HNO_3 for Co(II), Ni(II), Cu(II), and Zn(II). For Pt(II,IV), K_2PtCl_4 and Na_2PtCl_6 were also utilized. $Pd(OAc)_2$ and some Pd complexes such as $PdCl_2(PhCN)_2$ [8], $Pd_2(dba)_3$ [9], $PdCl_2(PEt_3)_2$ [10], and $PdCl_2(PPh_3)_2$ [11], which were prepared in accordance with the literature, were used to investigate Pd sorption in an organic solution.

IR, NMR, and mass spectra were recorded on a Jasco FT/IR-230 spectrometer, a JEOL JNM-α400 or Bruker AVANCE-600 NMR spectrometer, and a Shimadzu LCMS-2010 mass spectrometer, respectively. Elemental analyses were carried out using a Yanaco CHN Corder MT-5. To determine the metals in solutions, a Hitachi 180-80 polarized Zeeman

atomic absorption spectrometer and a PerkinElmer Optima 3000XL inductively coupled plasma atomic emission spectrometer were used.

2.2 Preparation of PTA

The preparation of poly(iminoterephthalthioyliminohexamethylene) (69% yield) was carried out in a manner analogous to that in our previous report (Scheme 1) [5]. The number average molecular weight, M_n, was 8800.

2.3 Preparation of Model Compound

N-isobutylthiobenzamide was prepared by the Willgerodt-Kindler reaction (87% yield) in accordance with the literature [12]. To a solution of *N*-isobutylthiobenzamide (386 mg, 2.0 mmol) in EtOH (5 mL), an aqueous solution (5 mL) of K_2PdCl_4 (162 mg, 0.5 mmol) was added. The solution was stirred for 24 h at room temperature. The organic fraction was evaporated, and the resulting orange precipitate was collected and thoroughly washed with water, hexane, and ether to give an orange powder of tetrakis(*N*-isobutylthiobenzamide-κ*S*)palladium(II) dichloride (461 mg, 96% yield). Crystals suitable for X-ray diffraction analysis were obtained after 3 days by slowly evaporating a mixture of EtOH and H_2O solution of the complex. Analysis calculated for $C_{44}H_{60}N_4Cl_2PdS_4 \cdot H_2O$: C 54.56, H 6.45, N 5.78%; found: C 54.35, H 6.28, N 5.69%. ESI-MS: 915, 913 ($\{[Pd(C_{11}H_{15}NS)_4]Cl\}^+$), 720, 722 ($\{[Pd(C_{11}H_{15}NS)_3]Cl\}^+$), 529, 527 ($\{[Pd(C_{11}H_{15}NS)_2]Cl\}^+$). IR (KBr, cm^{-1}): 3368, 3134, 2959, 2926, 1559, 1489, 1462, 1387, 1338, 1290, 1227, 1155, 1053, 999, 952, 933, 889, 770, 696, 536, 453, 418. ^1H NMR (500 MHz, CD_3OD): δ = 7.69 (t, 1H, *J* = 7.5 Hz), 7.51 (t, 2H, *J* = 7.5 Hz), 7.42 (t, *J* = 6.5 Hz), 3.42 (d, 2H, *J* = 7.2 Hz), 2.11 (sep, 1H, *J* = 6.7 Hz), 0.98 (d, *J* = 6.7 Hz). ^{13}C NMR (125 MHz,

CD_3OD): δ = 187.6, 131.1, 124.7, 120.6, 120.4, 47.2, 19.2, 5.69.

2.4 Procedure for Sorption and Elution of Metal

The sorption of the metal was carried out in glass vials. To aqueous and organic solutions (5-100 mL) containing an appropriate amount of metal or its complex (for Pd), HCl, NaOH solution, or MeONa was added to control the acidity or basicity in the solution. Powdered PTA was then added to the solution. After the solution was stirred vigorously using a magnetic stirrer, it was filtered through a membrane filter (Nihon Millipore, Omnipore membrane, 0.2 μm pore size). The percentage of metal sorption was calculated from the difference in the amount of metal in the solution before and after the sorption.

For Pd elution, the Pd-sorbed PTA was placed a grass vial containing MeOH or the other organic solvent (10-40 mL) with the filter. To the vial, a powdered tertiary phosphine compound was added. After stirring vigorously, the solution was filtered. The percentage of Pd elution was calculated from the amount of Pd in the filtrate.

2.5 X-ray Crystallographic Structure of Model Compound

The diffraction data were collected using a Rigaku Saturn CCD area detector with graphite monochromated MoKα (λ = 0.71070 Å) at –160 ºC. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied. The structure was solved by direct methods (SIR92) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically. Crystal data of tetrakis(*N*-isobutylthiobenzamide-κ*S*)palladium(II) dichloride: $C_{44}H_{64}N_4Cl_2PdS_4O$, M = 986.56, monoclinic, $P2_1/n$, a = 10.642(4), b = 17.138(6), c = 13.856(4) Å, β = 92.2275(18) °, V = 2525.1(14) Å^3, Z = 2, D_{calc} = 1.297 g cm^{-3}, μ(Mo-Kα) =

6.759 cm^{-1}, T = 113 K, $F(000)$ =1032, observed reflections 5561(all data), variables 387, R_1 = 0.0372, R_w = 0.0213, GOF = 0.884. Crystallographic data of the structural analysis have been deposited with the Cambridge Crystallographic Data Centre; Publication Number CCDC 699162.

3 Results and Discussion

3.1 Sorption Behavior of Pd, Ni, and Pt in Aqueous and Organic Solutions

The sorption behavior of various metals including the group 10 metals, Ni(II), Pd(II), and Pt(II,IV), was first investigated in aqueous solution to evaluate the potential of PTA for the selective sorption of Pd(II). Figure 1 shows the sorption behavior of PTA toward the metals at various pH. PTA exhibited excellent sorption behavior toward Pd(II); Pd(II) was effectively sorbed on PTA under not only acidic conditions but also basic conditions. In contrast, Ni(II) was hardly sorbed on PTA at a pH below 2. The percentage of Ni(II) sorption increased with increasing pH and reached almost 100% at a pH above 6.3. Similar sorption behavior was obtained for Co(II), Zn(II), and Cu(II); the percentages of sorption for these metals were less than 0.4% at pH 2 and more than 90% at pH 9-10. For Au(III) and Pt(II,IV), the opposite tendency was observed (Fig. 1). The quantitative sorption of Au(III), Pt(II), and Pt(IV) was observed below pHs of 3.9, 6.9, and 2.0, respectively; the sorption percentages decreased with increasing pH. These results indicate that PTA has the potential to selectively separate Pd(II) from Ni(II), Co(II), Zn(II), and Cu(II) under acidic conditions as well as from Pt(II,IV) and Au(III) under basic conditions.

Since PTA exhibited the attractive property of sorbing Pd(II), the sorption of Pd(II) was investigated in detail. The sorption of Pd(II) on PTA at pH 1 followed the Langmuir adsorption isotherm. The maximum amount of Pd(II) sorbable by 1 g of PTA was 1.03

mmol, corresponding to 0.287 mmol of Pd(II) sorbed by 1 mmol of the recurring unit in PTA (Scheme 1). This amount was almost equal to the sorbable amount of Pt(IV) (1.04 mmol g^{-1}) and approximately one-third of that of Au(III) (2.82 mmol g^{-1}).

As models of organic liquid waste, sorption tests on Pd(II), Ni(II), and Pt(II,IV) in MeOH were carried out. As shown in Fig. 2, the sorption of Pd(II) was not affected by the presence of HCl and MeONa; this tendency was similar to the sorption of Pd(II) in aqueous solution. The results for Ni(II) and Pt(II,IV) were also consistent with those in aqueous solution. The sorption was also investigated using various organic solutions of $Pd(OAc)_2$; the results are summarized in Table 1. More than 76% of Pd(II) was sorbed from the various model organic solutions, indicating that PTA has the ability to sorb Pd(II) from organic liquid waste.

3.2 Structure of Model Pd Complex

Secondary thioamides are easily deprotonated to give their anionic thionate form, in which the coordination potential is not only closer to that of a thiolate group but also further enhanced by the donor capacity of the nitrogen atom via the S-to-N backbone [6]. To elucidate the sorption capability of PTA toward Pd(II), we determined the molecular structure of a model compound.

A model complex ($[Pd(C_{11}H_{15}NS)_4]Cl_2$, **1**) was prepared from the reaction of *N*-isobutylthiobenzamide with K_2PdCl_4 in a mixture of EtOH and H_2O in accordance with the sorption experiments on PTA; reactions of K_2PdCl_4 with 2 and 4 equivalents of *N*-isobutylthiobenzamide produced the same product (**1**).

Figure 3 shows the ORTEP drawing of **1**. As shown in Fig. 3, the Pd atom of **1** is located at an inversion center, and the Pd(II) ion possesses a crystallographically imposed square planar geometry. Four *N*-isobutylthiobenzamide molecules serve as a monodentate

S-donor ligand in its thione tautomeric form, as illustrated by the scheme in Fig. 3. The thione form of the ligand has also been confirmed by ^{13}C NMR spectroscopy (δ 187.6). These results coincide with those reported for thioamide-ligated palladium complexes [13]. These results suggest that the presence of a S donor plays an important role in the sorption of Pd(II) by PTA.

3.3 Sorption Behavior of Various Pd Complexes in Organic Solutions

The sorption of various Pd complexes dissolved in organic solvents was attempted. The obtained results are shown in Table 2. When $PdCl_2(PhCN)_2$ was used for the test, quantitative sorption of Pd(II) was achieved for various organic solutions and their mixtures. In the case of $Pd_2(dba)_3$, which is one of the popular Pd(0) complexes, Pd was almost completely sorbed on PTA under acidic conditions; the sorption under neutral condition could not be determined because of its poor solubility in MeOH. These results indicate that Pd can be effectively sorbed from various organic solutions of these Pd complexes.

In contrast to $PdCl_2(PhCN)_2$ and $Pd_2(dba)_3$, low percentages of Pd sorption were observed for $PdCl_2(PEt_3)_2$ and $PdCl_2(PPh_3)_2$. The ineffective sorption appears to be due to the strong affinity of Pd(II) with phosphine ligands compared with that of the thioamide group. Thus, we oxidized the phosphine ligand before the sorption experiment by the addition of H_2O_2 to a $CHCl_3$ solution of $PdCl_2(PPh_3)_2$. The pretreatment was reasonably effective, and the percentage of Pd sorption increased to 41% (last row in Table 2). Further work is required to determine optimal conditions, but this result indicates that the vigorous oxidation of phosphine to phosphine oxide efficiently improves the recovery of Pd from a solution containing Pd complexes with phosphine ligands.

3.4 Elution and Reusability

The desorption of Pd(II) and the reuse of the sorbent are also crucial factors in the recovery processes of precious metals. As mentioned above, PTA was able to sorb hardly any Pd(II) from organic solutions of Pd-phosphine complexes. This result indicated to us that the Pd(II) sorbed on PTA can be eluted by the phosphine ligands. Figure 4 shows the results for the elution of Pd(II) sorbed on PTA using MeOH solutions containing various amounts of triphenylphosphine (TPP) and 1,3-bis(diphenylphosphino)propane (DPPP). In this experiment, the Pd(II)-sorbed PTA was prepared using MeOH solutions containing the Pd(II) standard solution and 20 mmol L^{-1} HCl. As shown in Fig. 4, TPP was able to elute up to 62% of the sorbed Pd(II), indicating that the P donor of TPP played an important role in the elution of Pd(II) from PTA. When DPPP was used as an eluent, the chelating effect of DPPP significantly improved the elution of Pd(II), and quantitative elution of Pd(II) was accomplished. In addition, we found that the addition of a small amount of HCl to the MeOH solution was efficient for achieving quantitative and reproducible elution of Pd(II) on PTA using DPPP, although the effect of HCl on the elution process is not clear at present. This elution technique was possible for every Pd-sorbed PTA sample prepared under various conditions; the tested samples were prepared using MeOH containing $PdCl_2(PhCN)_2$ and $CHCl_3$ containing $PdCl_2(PhCN)_2$ or $Pd(OAc)_2$. From these results, a combination of MeOH containing 20 mmol L^{-1} HCl and powdered DPPP was useful for the elution of Pd(II).

On the basis of these results, the reusability of PTA as a Pd sorbent was examined. Pd(II) was sorbed in MeOH containing 20 mmol L^{-1} HCl and then eluted using MeOH containing 20 mmol L^{-1} HCl and powdered DPPP; the sorption and elution were carried out repeatedly. As shown in Fig. 5, the sorption capability of PTA remained almost constant, and the quantitative sorption and elution can be achieved at least five times.

3.5 Demonstration of Separation of Pd from Ni or Pt

To evaluate the ability of PTA as a sorbent toward Pd(II), the selective separation of Pd(II) from MeOH solution containing Ni(II) was carried out. Since Ni(II) was scarcely sorbed on PTA from acidic MeOH solution (Fig. 2), the sorption was investigated using MeOH solutions containing 20 mmol L^{-1} HCl and both Pd(II) and Ni(II). As shown in Table 3, PTA only sorbed Pd(II) from the solution; note that the selective separation of Pd(II) was achieved from a MeOH solution containing a large amount of Ni(II) of up to 100 times higher than that of Pd(II). Over 94% of the sorbed Pd(II) was recovered.

The separation of Pd(II) from MeOH solution containing Pt(IV) was also investigated. Since Pt(IV) was hardly sorbed under basic conditions (Fig. 2), the sorption was carried out using MeOH solutions containing 50 mmol L^{-1} MeONa and both Pd(II) and Pt(IV). The obtained results are summarized in Table 4. The quantitative sorption of Pd(II) was observed for the solution containing a 10 times larger amount of Pt(IV) than that of Pd(II), and 84% of Pd(II) was sorbed even from a solution containing 100 times more Pt(IV). In these cases, Pt(IV) was hardly sorbed on PTA, and the elution of Pt(IV) was negligible. The sorbed Pd(II) was quantitatively eluted. The separation of Pd(II) from Pt(II) was not examined because a black precipitate was formed when both Pd(II) and Pt(II) were added to MeOH solution containing MeONa. These results indicate that PTA is an effective sorbent enabling the selective separation and recovery of Pd(II) from a solution also containing a large amount of Ni(II) and Pt(IV).

4 Conclusions

PTA has the ability to sorb Pd in various organic solutions under not only acidic conditions but also basic conditions. The Pd sorbed on PTA could be eluted quantitatively in MeOH using DPPP as an eluent. Since Ni(II) and Pt(IV) were hardly sorbed under acidic conditions

and basic conditions, respectively, the selective separation of Pd(II) from Ni(II) or Pt(IV) was achieved by controlling the acidity or basicity of the solution. To our knowledge, this is the first example of the effective separation of Pd(II) from an organic solution containing a large amount of Ni(II) and Pt(IV). PTA is thought to contribute to the separation and recovery of Pd, which is utilized as a catalyst in various chemical processes.

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References

1. (a) E. Negishi (ed), Handbook of Organopalladium Chemistry for Organic Synthesis, vol. I&II. Wiley, New York (2002); (b) L. Brandsma, S. F. Vasilevsky, H. D. Verkruijsse, Application of Transition Metal Catalysts in Organic Synthesis. Springer, Berlin (1998).
2. (a) N. E. Leadbeater, M. Marco, Chem. Rev. **102**, 3217 (2002); (b) C. A. McNamara, M. J. Dixon, M. Bradley, Chem. Rev. **102**, 3275 (2002); (c) N. T. S. Pham, M. Van der Sluys, C. W. Jones, Adv. Synth. Catal. **348**, 609 (2006).
3. (a) K. Oshita, S. Motomizu, Bunseki Kagaku **57**, 291 (2008); (b) M. V. Dinu, E. S. Dragan in E. S. Dragan (ed), New Trends in Ionic (Co) Polymers and Hybrids. Nova Publishers, New York (2007); (c) E. Guibal, Sep. Purif. Technol. **38**, 43 (2004); (d) L. Dambies, Sep. Sci. Technol. **39**, 603 (2004); (e) T. P. Rao, C. R. Preetha, Sep. Purif. Rev. **32**, 1 (2003); (f) R. Chiarizia, E. P. Horwitz, S. D. Alexandratos, M. J. Gula, Sep. Sci. Technol. **32**, 1 (1997); (g) C. Kantipuly, S. Katragadda, A. Chow, H. D. Gesser, Talanta **37**, 491 (1990).
4. K. Ishihara, M. Nakayama, H. Kurihara, A. Itoh, and H. Haraguchi, Chem. Lett. 1218 (2000).

5. T. Kanbara, Y. Kawai, K. Hasegawa, H. Morita, T. Yamamoto, J. Polym. Sci., Part A: Polym. Chem. **39**, 3739 (2001).
6. J. Sola, A. López, R. A. Coxall, W. Clegg, Eur. J. Inorg. Chem. 4871 (2004).
7. S. Kagaya, E. Sato, I. Masore, K. Hasegawa, T. Kanbara, Chem. Lett. **32**, 622 (2003).
8. J. R. Doyle, P. E. Slade, H. B. Jonassen, Inorg. Synth. **6**, 218 (1960).
9. T. Ukai, H. Kawazura, Y. Ishii, J. Organomett. Chem. **65**, 253 (1974).
10. F. G. Mann, D. Purdie, J. Chem. Soc. 1549 (1935).
11. J. Chatt, F. G. .Mann, J. Chem. Soc. 1622 (1939).
12. E. V. Brown, Synthesis **1975**, 358.
13. (a) A. J. Aarts, H. O. Desseyn, M. A. Herman, Bulletin des Societes Chimiques Belges **88**, 25 (1979); (b) Y. Nojima, M. Nonoyama, Polyhedron **15**, 3795 (1996); (c) R. A. Begum, D. Powell, K. Bowman-James, Inorg. Chem. **45**, 964 (2006); (d) M. Akaiwa, T. Kanbara, H. Fukumoto, T. Yamamoto, J. Organomet. Chem. **690**, 4192 (2005); (e) K. Okamoto, T. Kanbara, T. Yamamoto, Chem. Lett. **35**, 558 (2006).

Table 1 Sorption of Pd(II) in some organic solutions on PTA

Solution	Sorption / %
MeOH	100
$CHCl_3$	98
Toluene	82
Acetone	76
MeCN	88
EtOAc	77

$Pd(OAc)_2$ (1 μmol) was added to 10 mL of the solution. PTA, 5 mg; stirring, 6 h.

Table 2 Sorption of Pd complexes in some organic solution on PTA

Pd complex	Solution	Sorption / %
$PdCl_2(PhCN)_2$	MeOH	100
	MeOH + HCl [a]	100
	$CHCl_3$	100
	Toluene	100
	$CHCl_3$ + Acetone (1 + 1)	100
	Toluene + Acetone (1 + 1)	100
$Pd_2(dba)_3$	MeOH + HCl [a]	100
	$CHCl_3$	69
	$CHCl_3$ + Acetone (1 + 1)	96
$PdCl_2(PEt_3)_2$	MeOH	20
	MeOH + HCl [a]	24
	$CHCl_3$	16
	Toluene	0
	$CHCl_3$ + Acetone (1 + 1)	14
	Toluene + Acetone (1 + 1)	0
$PdCl_2(PPh_3)_2$	$CHCl_3$	19
	$CHCl_3$ [b]	41

Solution volume, 10 mL; Pd complex, 1 μmol; PTA, 5 mg; stirring, 6 h.

[a] MeOH containing 20 mmol L^{-1} HCl.

[b] $CHCl_3$ solution (20 mL) was stirred vigorously for 1 h with H_2O_2 (0.2 mL); 10 mL of the $CHCl_3$ solution was used for the sorption.

Table 3 Separation of Pd(II) from Ni(II)

Initial amount / μmol		Sorption / μmol		Elution / μmol	
Pd(II)	Ni(II)	Pd(II)	Ni(II)	Pd(II)	Ni(II)
1	1	1.00	0	1.00	0
1	10	1.00	0	1.00	0
1	100	1.00	0	0.94	0

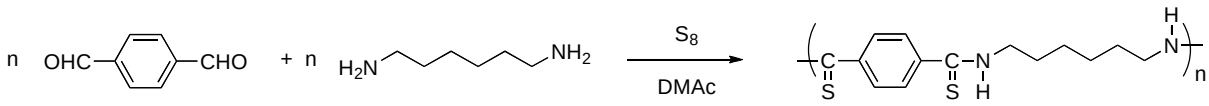
Sorption: Solution, 10 mL of MeOH containing 20 mmol L^{-1} HCl; PTA, 5 mg; stirring, 15 h. Elution: Solution, 10 mL of MeOH containing 20 mmol L^{-1} HCl; powdery DPPP, 5 μmol; stirring, 6 h.

Table 4 Separation of Pd(II) from Pt(IV)

Initial amount / μmol		Sorption / μmol		Elution / μmol	
Pd(II)	Pt(IV)	Pd(II)	Pt(IV)	Pd(II)	Pt(IV)
1	1	0.98	0	1.00	0
1	10	0.97	0.00_8	0.99	0.00_4
1	100	0.84	0.03_8	0.83	0

Sorption: Solution, 10 mL of MeOH containing 50 mmol L^{-1} MeONa; PTA, 5 mg; stirring, 15 h. Elution: Solution, 10 mL of MeOH containing 20 mmol L^{-1} HCl; powdery DPPP, 5 μmol; stirring, 6 h.

Scheme



Scheme 1 Preparation of PTA

Figure captions

Fig. 1 Effect of pH on the sorption of some metals in aqueous solution.
Solution volume, 10 mL; each metal, 1 μmol; PTA, 5 mg; stirring, 6 h.

Fig. 2 Sorption of Pd(II), Ni(II), and Pt(II,IV) in MeOH on PTA. Solution volume, 10 mL; Pd(II), Ni(II), or Pt(II,IV), 1 μmol; PTA, 5 mg; stirring, 15 h. A: MeOH containing 20 mmol L^{-1} HCl. B: MeOH only. C: MeOH containing 50 mmol L^{-1} MeONa.

Fig. 3 Molecular structure of **1**.

Fig. 4 Effect of the concentration of TPP (●) or DPPP (○) on the elution of Pd sorbed on PTA. Sorption: Solution, 5 mL of MeOH containing 20 mmol L^{-1} HCl and 1 μmol of Pd(II); PTA, 5 mg; stirring, 15 h. Elution: Solution, 10 mL of MeOH containing TPP and DPPP; stirring, 6 h.

Fig. 5 Reusability of PTA as Pd sorbent.
Sorption: Solution, 20 mL of MeOH containing 20 mmol L^{-1} HCl and 4 μmol of Pd(II); PTA, 20 mg; stirring, 15 h. Elution: Solution, 40 mL of MeOH containing 0.5 mmol L^{-1} DPPP; stirring, 6 h.

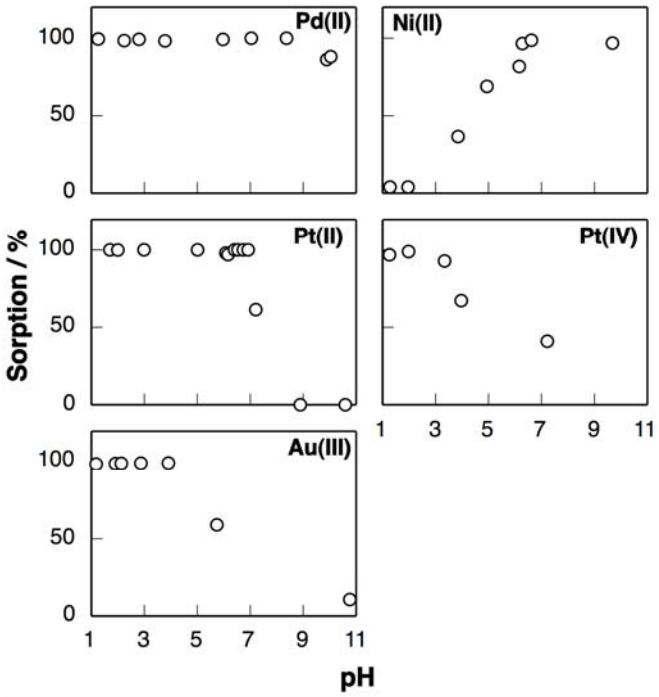


Fig. 1 S. Kagaya, E. Tanaka, N. Kawai, I. Masore, E. Sato, K. Hasegawa, M. Kishi, T. Kanbara

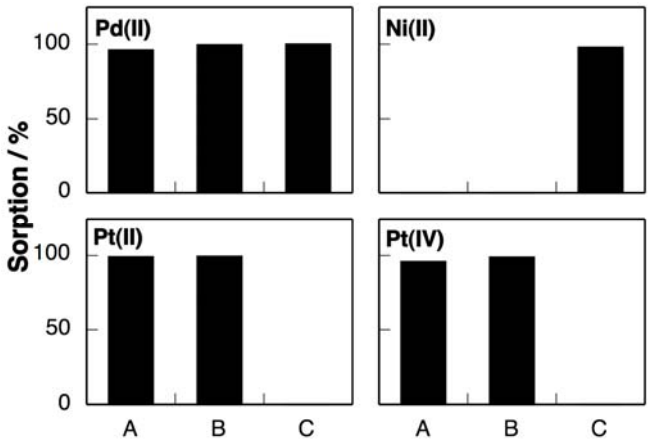


Fig. 2 S. Kagaya, E. Tanaka, N. Kawai, I. Masore, E. Sato, K. Hasegawa, M. Kishi, T. Kanbara

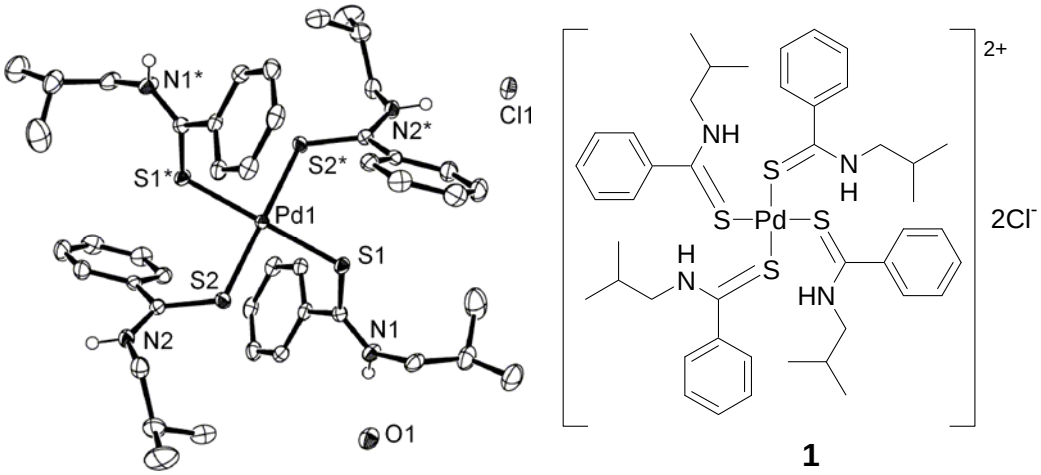


Fig. 3 S. Kagaya, E. Tanaka, N. Kawai, I. Masore, E. Sato, K. Hasegawa, M. Kishi, T. Kanbara

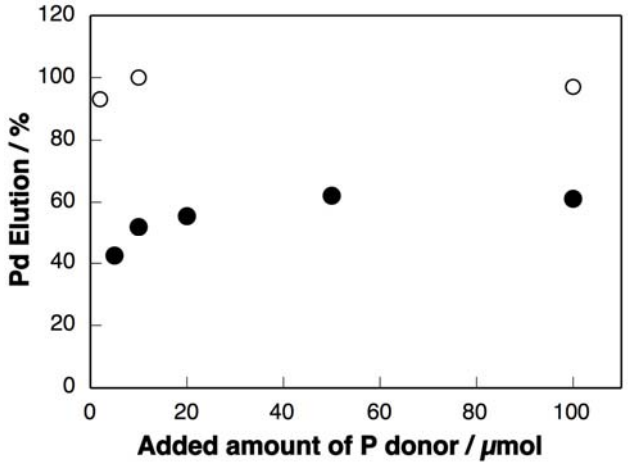


Fig. 4 S. Kagaya, E. Tanaka, N. Kawai, I. Masore, E. Sato, K. Hasegawa, M. Kishi, T. Kanbara

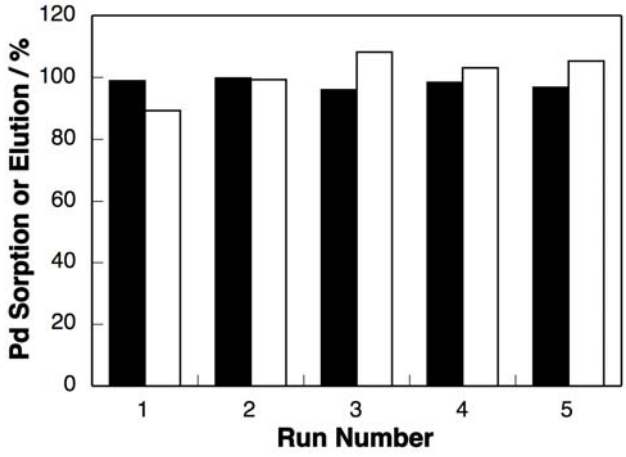


Fig. 5 S. Kagaya, E. Tanaka, N. Kawai, I. Masore, E. Sato, K. Hasegawa, M. Kishi, T. Kanbara